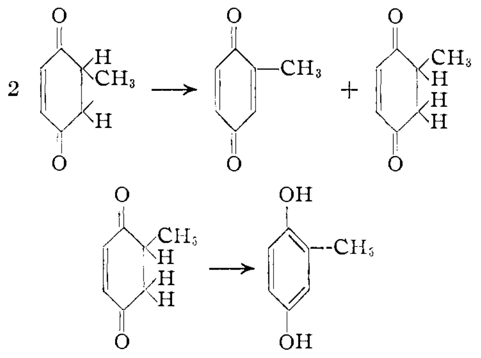
**Products of Reaction.**—It is assumed that $Q\cdot CH_3$ is the first product of the reaction involving a quinone and methyl radicals; however, $Q\cdot CH_3$ cannot be the final product of the reaction. The final product of the reaction must result from the interaction involving either two $Q\cdot CH_3$ species or $Q\cdot CH_3$ and iso-$C_8H_{17}$ radicals. It seems improbable that $Q\cdot CH_3$ would react with another methyl radical since, if that were the case, then one would expect an increase in $k_{II}/k_I$ for a decreasing $X_Q$, contrary to experimental findings.

Unsuccessful attempts were made to isolate and identify the final product of the reaction. The reaction with *p*-benzoquinone in isoöctane yields a purple compound, which precipitates on cooling the solvent to about −15°. This compound can be dissolved again in various solvents including water the solution, however, being yellow. On analysis, it is found however, that the compound contains "active" hydrogen, suggesting the presence of hydroxylic group. This might indicate the occurrence of reactions such as



or

$$Q\cdot CH_3 + \text{iso-}C_8H_{17} \longrightarrow Q\cdot H\cdot CH_3 + \textit{iso-}C_8H_{16}$$

In conclusion, we would like to thank the National Science Foundation for financial support of this research.

SYRACUSE, N. Y.

---

[CONTRIBUTION FROM THE CHEMICAL AND RADIOLOGICAL LABORATORIES]

# Hydrogen Bonding of Phosphoryl Compounds with Chloroform and Other Solvents

BY ERNEST HALPERN, JAMES BOUCK, HAROLD FINEGOLD AND JEROME GOLDENSON

RECEIVED MARCH 10, 1955

The hydrogen bonding of $POCl_3$, $(C_2H_5O)_3PO$ and $(n\text{-}C_4H_9)_3PO$ with chloroform, pentachloroethane, *sym*-tetrachloroethane and *n*-heptane was studied by means of infrared spectroscopy. The order of hydrogen bonding of the phosphoryl compounds was as follows: $(n\text{-}C_4H_9)_3PO > (C_2H_5O)_3PO > POCl_3$. The order of hydrogen bonding of the solvents was: $CHCl_3 > CHCl_2\text{–}CCl_3 > CHCl_2\text{–}CHCl_2 >> n\text{-}C_7H_{16}$ (none).

## Introduction

From a determination of the differences in the heat of mixing of chloroform with fifteen phosphoryl compounds, Kosolapoff and McCullough[1] found that hydrogen bonding is increased by replacement of groups attached to the phosphorus atom in the order of $Cl < OR < R$, and concluded that the hydrogen bonding ability is enhanced with increased electron density at the central group. Progressive increases in hydrogen bonding were shown as in the following series: $POCl_3 < ROP(O)Cl_2 < (RO_2)P(O)Cl < (RO)_3PO < RP(O)(OR')_2 < R_2P(O)(OR)$. Previous work on the hydrogen bonding of the C–H linkage is given in references 2 to 11.

In the work described in this paper, the association of phosphorus oxychloride, triethyl phosphate and tri-*n*-butyl phosphine oxide with chloroform, *sym*-tetrachloroethane, pentachloroethane and *n*-heptane was studied by means of infrared spectroscopy. Absorption bands due to the P=O and P–O–C (in the case of triethyl phosphate) linkages were investigated as well as the C–H linkage of the chloroform and other acceptor solvents. Evidence of association of the hydrogen bonding type was found with all the chlorinated acceptor solvents, but not with *n*-heptane. By determination of the changes in the integrated absorption intensities of the C–H band, the order of hydrogen bonding strengths of the acceptor solvents for phosphorus oxychloride, triethyl phosphate and tri-*n*-butyl phosphine oxide was found to be as follows: $CHCl_3 > CHCl_2\text{–}CCl_3 > CHCl_2\text{–}CHCl_2 \gg n\text{-}C_7H_{16}$ (none). The order of hydrogen bonding strengths of the phosphoryl compounds for the acceptor solvents was confirmed[1] to be as follows: $(n\text{-}C_4H_9)_3PO > (C_2H_5O)_3PO > POCl_3$.

**Equipment.**—A Perkin–Elmer model 12C equipped with a lithium fluoride prism was used to study the C–H absorption bands (fundamentals) of the acceptor solvents. A Perkin–Elmer model 21 with sodium chloride optics was used to study the P=O absorption band of the phosphoryl compounds.

**Purification of Materials.** $CHCl_3$.—Since the alcohol used as a stabilizer in chloroform would interfere with hydrogen bonding studies, it was removed by washing with water. The chloroform was then dried over calcium chloride and the infrared spectrum determined to ensure that the O–H absorption peak of the alcohol was removed.

---

[1] G. M. Kosolapoff and J. F. McCullough, THIS JOURNAL, **73**, 5392 (1951).

[2] D. B. MacLeod and F. J. Wilson, *Trans. Faraday Soc.*, **31**, 596 (1935).

[3] S. Glasstone, *ibid.*, **33**, 200 (1937).

[4] R. H. Ewell, *J. Chem. Phys.*, **5**, 967 (1937).

[5] W. Gordy, THIS JOURNAL, **60**, 605 (1938).

[6] A. M. Buswell, W. H. Rodebush and M. F. Roy, *ibid.*, **60**, 2528 (1938).

[7] M. J. Copley, G. F. Zellhoefer and C. S. Marvel, *ibid.*, **60**, 2666 (1938).

[8] W. Gordy, *J. Chem. Phys.*, **7**, 163 (1939).

[9] C. S. Marvel, M. J. Copley and E. Ginsberg, THIS JOURNAL, **62**, 3109 (1940).

[10] L. F. Audrieth and R. Steinman, *ibid.*, **63**, 2115 (1941).

[11] C. M. Huggins and G. C. Pimentel, Paper presented at Symposium on Molecular Structure and Spectroscopy, The Ohio State University, Columbus, 14–18, June 1954.

TABLE I

INTEGRATED ABSORPTION INTENSITIES OF C–H BAND OF ACCEPTOR SOLVENTS[a]

| | Phosphoryl compound | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | POCl$_3$ | | | | (C$_2$H$_5$O)$_3$PO | | | | ($n$-C$_4$H$_9$)$_3$PO | | | |
| Acceptor solvent | $A$ (cycles × l.)/(moles × cm.) | $A^1$ | $\Delta A$ | $(\Delta A/A^1) \times 100$ | $A$ (cycles × l.)/(mole × cm.) | $A^1$ | $\Delta A$ | $(\Delta A/A^1) \times 100$ | $A$ (cycles × l.)/(mole × cm.) | $A^1$ | $\Delta A$ | $(\Delta A/{}^1A) \times 100$ |
| CHCl$_3$ | 790 | 540 | 250 | 46 | 2185 | 603 | 1582 | 263 | 3460 | 348 | 3112 | 995 |
| CHCl$_2$CCl$_3$ | 1410 | 1270 | 140 | 11 | 1712 | 567 | 1145 | 202 | 4350 | 975 | 3375 | 346 |
| CHCl$_2$CHCl$_2$ | 1435 | 1344 | 91 | 7 | 2560 | 1565 | 995 | 64 | 3920 | 1210 | 2710 | 224 |
| $n$-C$_7$H$_{16}$ | .. | .. | 0 | 0 | 36600 | 36300 | 300 | 1 | 41900 | 43100 | −1200 | −3 |

[a] 4/1 moles of acceptor solvent to phosphoryl compound.

Chloroform purified in this manner was found to be stable for about five days at room temperature.

POCl$_3$.—Phosphorus oxychloride was purified by fractional distillation. Its infrared spectrum was checked for the desired degree of purity.

(C$_2$H$_5$O)$_3$PO.—Triethyl phosphate could not be purified by fractional distillation. The O–H fundamental stretching vibration absorption band of the acid was found in the spectrum of the distillate. The acid impurity was eliminated by treatment with calcium hydride.

Pentachloroethane, *sym*-tetrachloroethane and *n*-heptane were purified by fractional distillation. The spectra of these solvents were compared with their known spectra and found to be satisfactory.

CCl$_4$.—Eastman Kodak Co. Organic Chemicals Spectro Grade carbon tetrachloride was used as the solvent.

## Experimental

The bonded C–H absorption of the acceptor solvents was obtained by difference between the spectra of solutions of 1.25 moles/l. of acceptor solvent and 0.31 mole/l. of phosphoryl compound in carbon tetrachloride and 0.31 mole/l. of phosphoryl compound in carbon tetrachloride. The resulting C–H absorption was then compared with the C–H absorption of a solution of 1.25 moles/l. of acceptor solvent in carbon tetrachloride. The spectra were obtained under the same conditions of slit width,[12] gain, speed and cell thickness.

## Data and Discussion

The integrated absorption intensity,[13] $A$, is defined as

$$A = 1/cl \int \ln (I_0/I) \mathrm{d}v$$

$c$ = concn. in moles/liter
$l$ = cell length in cm.
$\ln (I_0/I)$ = optical density
$v$ = frequency, cm.$^{-1}$

where the integral is integrated over the limits of the C–H stretching fundamental band. The zero level of hydrogen bonding in the acceptor solvents was set by the integrated absorption intensity, $A'$, of the C–H band in the absence of the phosphoryl compound. $A$ is defined as the integrated absorption intensity of the C–H band of the acceptor solvents in the presence of the phosphoryl compound. The difference $A - A' = \Delta A$ is the deviation from the Beer–Lambert law. The slit width error is cancelled out since $A$ and $A'$ were determined at the same slit width. The function $\Delta A/A' \times 100$ was used to determine the relative hydrogen bonding strengths of the acceptor solvents and of the phosphoryl compounds.

Data obtained on the C–H stretching fundamental vibrations are summarized in Table I. It may be noted in this table that the $\Delta A/A' \times 100$ values for the phosphoryl compounds are in the order ($n$-C$_4$H$_9$)$_3$PO > (C$_2$H$_5$O)$_3$PO > POCl$_3$. This is in agreement with the heat of mixing data.[1] The $\Delta A/A' \times 100$ values for the acceptor solvents indicate the following order of hydrogen bonding

$$\mathrm{CHCl_3} > \mathrm{CHCl_2{-}CCl_3} > \mathrm{CHCl_2{-}CHCl_2} >> n\text{-}\mathrm{C_7H_{16}}\ (\text{none})$$

Buswell, Rodebush and Roy[6] found a threefold increase in intensity of the C–H absorption band in the CHCl$_3$–quinoline system. Huggins and Pimentel[11] found that the C–D band is twenty times more intense when CDCl$_3$ is dissolved in acetone than in CCl$_4$. The same type of increase in C–H absorption intensity was observed for the chlorinated solvents in POCl$_3$ and (C$_2$H$_5$O)$_3$PO. But for tri-*n*-butylphosphine oxide the C–H absorption band of the chlorinated solvents was shifted toward lower frequency (Table II).

TABLE II

POSITION OF C–H BANDS OF ACCEPTOR SOLVENTS

| | | Phosphoryl compd. and acceptor solvent in CCl$_4$ soln. | | |
|---|---|---|---|---|
| Acceptor solvent | CCl$_4$ soln. alone, cm.$^{-1}$ | POCl$_3$, cm.$^{-1}$ | (C$_2$H$_5$O)$_3$PO, cm.$^{-1}$ | ($n$-C$_4$H$_9$) PO, cm.$^{-1}$ |
| CHCl$_3$ | 2998 | 2998 | 2998 | 2935 b[a] |
| CHCl$_2$–CCl$_3$ | 2965 | 2965 | 2965 | 2963 |
| | | | 2940 b[a] | 2895 b[a] |
| CHCl$_2$–CHCl$_2$ | 2960 | 2960 | 2960 | 2960 |
| | | | | 2925 b[a] |
| $n$-C$_7$H$_{16}$ | 2937 | No shift | No shift | No shift |
| | 2907 | | | |
| | 2860 | | | |
| | 2843 | | | |

[a] b, broad.

In the case of the CHCl$_2$CCl$_3$–(C$_2$H$_5$O)$_3$PO mixture, the C–H fundamental band was split into a doublet with peaks at 2940 and 2965 cm.$^{-1}$. The new band at 2940 cm.$^{-1}$ was found to have an area 1.8 times the 2965 cm.$^{-1}$ band. The value of $A$ given in Table I was taken as the sum of the areas of these bands. The same procedure was followed for the acceptor solvents and ($n$-C$_4$H$_9$)$_3$PO mixtures. The shifted C–H bands of the acceptor solvents are listed in Table II.

**The P=O and P–O–C Absorption Bands for Phosphoryl Compounds.**—The P=O absorption band of the phosphoryl compounds in the presence of the chlorinated solvents shifts about 2 cm.$^{-1}$ for POCl$_3$, 2 to 4 cm.$^{-1}$ for (C$_2$H$_5$O)$_3$PO and 8 cm.$^{-1}$ for ($n$-C$_4$H$_9$)$_3$PO (see Table III). The P=O absorption band in the presence of the chlorinated acceptor solvents is also broadened, but shows no change for *n*-heptane. The P–O–C band of the triethyl phosphate in the presence of the chlorinated solvents undergoes a slight shift toward higher

---

[12] A. R. Philpotts, W. Thain and P. G. Smith, *Anal. Chem.*, **23**, 268 (1951).

[13] R. N. Jones and K. Dobriner, "Infrared Spectrometry Applied to Steroid Structure and Metabolism," "Vitamins and Hormones," Vol. 7, Academic Press, Inc., New York, N. Y., 1949, p. 330.

frequency, but shows no change in the presence of *n*-heptane. However, the shifts of the P=O band to lower frequency (bond weakened) and the P–O–C band to higher frequency (bond strengthened) are in the direction which would be expected for hydrogen bonding to the phosphoryl oxygen.

TABLE III

POSITION OF P=O BANDS OF PHOSPHORYL COMPOUNDS

| | | Phosphoryl compd. and acceptor solvent in $CCl_4$ soln.[a] | | | |
|---|---|---|---|---|---|
| Phosphoryl compd. | $CCl_4$ soln. alone, cm.$^{-1}$ | $CHCl_3$, cm.$^{-1}$ | $CHCl_2$–$CCl_3$, cm.$^{-1}$ | $CHCl_2$–$CHCl_2$, cm.$^{-1}$ | $n$-$C_7H_{16}$, cm.$^{-1}$ |
| $POCl_3$ | 1305 | 1302 | 1303 | 1302 | 1305 |
| $(C_2H_5O)_3PO$ | 1263[c]<br>1275[c] | 1260<br>1271 (sh)[d] | 1260<br>1274 (sh)[d] | 1265[b] | 1263[c]<br>1275[c] |
| $(n$-$C_4H_9)_3PO$ | 1168 | 1160 | 1160 | 1160 | 1168 |

[a] 4/1 moles of acceptor solvent to phosphoryl compound. [b] Broad band. [c] Band of doublet. [d] Shoulder.

The fact that $(n\text{-}C_4H_9)_3P{=}O$ shows a greater shift of the P=O absorption band on hydrogen bonding with $CHCl_3$ than do $(C_2H_5O)_3P{=}O$ and $POCl_3$ indicates that the oxygen atom of the phosphoryl group has a variable negative charge, this charge being greatest in the trialkyl phosphine oxide.

It was mentioned in a previous paper[14] that trialkylphosphine oxides hydrogen bond with catechol and phenol. The shifts in the phosphoryl absorption due to hydrogen bonding with a hydroxyl hydrogen are greater than shifts in phosphoryl absorption due to hydrogen bonding with the hydrogen of a C–H group.

---

[14] J. V. Bell, J. Heisler, H. Tannenbaum and J. Goldenson, THIS JOURNAL, **76**, 5189 (1954).

ARMY CHEMICAL CENTER, MARYLAND

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

# Acid–Base Reactions in Non-dissociating Solvents. Acetic Acid and Diethylamine in Carbon Tetrachloride and Chloroform

BY E. ANNE YERGER AND GORDON M. BARROW

RECEIVED MARCH 21, 1955

The reactions between acetic acid and diethylamine in carbon tetrachloride and chloroform were studied by infrared spectroscopy. Structures for the various ion-pair products have been deduced from the observed spectral changes. These are discussed in terms of their expected stabilities. As in the triethylamine–acetic acid system, interaction with chloroform molecules greatly alters the electronic structure of the ion pairs. Equilibrium constants were determined for several of the reactions and were compared with previous results.

The reactions of organic acids and bases in non-dissociating solvents produce ion-pair products.[1,2,3] The use of infrared spectroscopy allows the extent of the acid–base reaction to be followed, and therefore equilibrium constants to be obtained, and the nature of the ion-pairs to be deduced. The latter is concerned with the number of species present in the ion-pair, the manner in which the ions are linked, and the role of the solvent in the ion-pair. Furthermore, infrared spectroscopy is applicable to a wide range of acids and bases and is not restricted to compounds with convenient absorption bands in the visible region.[4,5]

A previous study of the system of acetic acid and triethylamine[6] has shown that the association between ion-pairs is a specific interaction, leading to particular hydrogen bonded structures, rather than only a general electrostatic attraction. A relatively strong interaction of the ion-pair with a hydrogen bonding solvent molecule was also observed to lead to a specific structure. The role of such solvents cannot, therefore, be understood in terms of the dielectric constants alone.

It is of interest now to investigate the ion-pair species, their structures and the equilibrium constants for the reaction of acetic acid with a secondary amine. Structural features rather different from those encountered with a tertiary amine are to be expected. The diethylamine–acetic acid system is chosen as a model for reactions involving secondary amines with carboxylic acids. Diethylamine and acetic acid are spectroscopically convenient. Carbon tetrachloride is taken as a completely non-interacting solvent and the effect of a hydrogen bonding solvent is studied using chloroform. Equilibrium constants are calculated to test the validity of the proposed species and are compared with previous results.

## Experimental

The spectra discussed were obtained using a Baird Associates instrument with rock salt optics. Only the intensities of fairly low absorptions were used for quantitative work so that Beer's law could be assumed without appreciable error. The rock salt cells were 0.089 and 0.103 mm. thick, as determined by interference patterns, and 1.10, 9.3, 10.67 and 20.6 mm. thick, by direct measurement with a micrometer. The temperature of the samples was not controlled and was between room temperature, 25°, and that of the instrument, 30°.

The acetic acid, carbon tetrachloride and chloroform were purified as previously described.[6] The other reagents were prepared and purified as follows:

**Diethylamine:** Eastman Kodak white label diethylamine was dried over KOH and distilled. The constant boiling fraction at 55.6° was stored over KOH.

**Diethylammonium acetate:** equimolar quantities of diethylamine and acetic acid were mixed and cooled in an ice-bath. The resulting crystals, m.p. 26°, were dried under vacuum.

**Diethyldideuteroammonium acetate:** diethylammonium acetate was exchanged under vacuum with two samples of

---

[1] M. M. Davis and E. A. McDonald, *Bur. Standards J. Research*, **42**, 595 (1949).

[2] A. A. Maryott, *ibid.*, **41**, 1, 7 (1948).

[3] R. M. Fuoss and C. A. Kraus, THIS JOURNAL, **55**, 3614 (1933).

[4] M. M. Davis and H. B. Hetzer, *Bur. Standards, J. Research*, **48**, 381 (1952), and references to previous work.

[5] R. P. Bell and J. W. Bayles, *J. Chem. Soc.*, 1518 (1952).

[6] G. M. Barrow and E. A. Yerger, THIS JOURNAL, **76**, 5211 (1954).